solvate. Mo–Mo bond lengths and average torsional angles in these two species are 2.150 (3) Å and 24.6 [5]° for the THF solvate and 2.143 (2) Å and 22.9 [3]° for the CH_3CN solvate. Since no significant change in Mo–Mo distance (0.007 ± 0.005 Å) or χ (1.7 ± 8°) is observed, the differences in packing forces between one THF molecule and four CH_3CN molecules per dimer have essentially no effect on the structural parameters of interest.

Since the assumptions and approximations made in this study have been discussed in detail, some internal consistencies are deserving of brief mention. The fact that the small increases in the Mo–Mo bond distances in β-$Mo_2Cl_4(dmpe)_2$, β-$Mo_2Br_4(dmpe)_2$, and β'-$Mo_2Cl_4(dmpe)_2$ all correlate with the small increases in χ is excellent support for a monotonic relationship between these two variables. The behavior of these three compounds is particularly important because the ligand dmpe is the same in all three. It is also satisfying that the observed differences in χ between analogous molybdenum and rhenium dimers may be explained by different bond multiplicities. In the $M_2Cl_4(dppe)_2$ case, χ = 34.0 [6]° for M = Re and 30.5 [5]° for M = Mo. The difference of 3.5° results from the absence of δ bonding (i.e., an absence of resistance to rotation) in the rhenium complex and the presence of ca. half of a δ bond in the molybdenum complex. In the Re dimer, the amount of staggering is determined entirely by the conformational preferences of the bridging moiety, while in the Mo dimer, δ bonding resists the preferences of the PP ligands. For the $M_2Cl_4(depe)_2$ case, the difference in χ is smaller: 43.7 (4)° with M = Re and 42.7 (4)° with M = Mo. This is the predicted result since now the bond order of the Mo complex is ca. 3.1 or almost the same as the Re complex.

The new value, 0.097 Å, for the change in Mo–Mo bond length upon total loss of δ bonding (but without any change in atomic charges) is more consistent with other information than was the previous estimate (from Figure 1b) of ca. 0.06 Å. The best independent indications of the distance change for Mo–Mo bonds are obtained from the Franck–Condon factors in the vibrational progressions for $\delta \rightarrow \delta^*$ transitions in $Mo_2(O_2CCH_3)_4$ and $Mo_2Cl_8^{4-}$. In both cases[13] the result is 0.11 ± 0.01 Å.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. **1**, 99033-20-2; **2**, 99033-21-3; $K_4Mo_2Cl_8$, 25448-39-9; $(n\text{-}Bu_4N)_2Re_2Cl_8$, 14023-10-0; Mo, 7439-98-7; Re, 7440-15-5.

Supplementary Material Available: Tables of structure factors and displacement vibration parameters and complete lists of bond lengths and angles for both compounds (14 pages). Ordering information is given on any current masthead page.

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Vanadium(II) and Niobium(III) Edge-Sharing Bioctahedral Complexes That Contain Bis(dimethylphosphino)methane Bridges

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Two compounds, each containing bis(dimethylphosphino)methane (dmpm) bridges, have been prepared from $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$ and $Nb_2(\mu\text{-}Cl)_2(\mu\text{-}THT)Cl_4(THT)_2$, respectively, and characterized completely via single-crystal X-ray studies. The vanadium compound, $[VCl(dmpm)BH_4]_2$ (**1**), is dinuclear and adopts an edge-sharing bioctahedral structure with two bridging dmpm units, two bridging chlorine atoms, and two borohydride ligands occupying axial V–V positions. The V–V distance of 3.124 (2) Å suggests that little, if any, direct metal–metal bonding occurs between the two vanadium atoms. This compound crystallizes in space group *Pbca* with the following unit cell dimensions: a = 12.395 (3) Å, b = 14.163 (3) Å, c = 13.858 (4) Å, V = 2433 (2) Å^3, Z = 4. The niobium complex, $Nb_2Cl_6(dmpm)_2$ (**2**), also consists of two octahedra sharing an edge, with two dmpm bridges, two bridging chlorine atoms, and four terminal chlorine ligands. The Nb–Nb distance equals 2.711 (3) Å, which is consistent with a $\sigma^2\pi^2$ double bond between the two niobium atoms. For **2**, crystallographic data are as follows: $P2_1/n$, a = 7.214 (3) Å, b = 15.468 (7) Å, c = 10.828 (5) Å, β = 93.6 (4)°, V = 1205 (2) Å^3, Z = 2. An explanation for the different structures of the $Nb_2Cl_6(dmpm)_2$ and $Nb_2Cl_6(dppm)_2$ molecules based on a proposed mechanism of formation and solubility differences is offered.

Introduction

The ability of bis(diphenylphosphino)methane (dppm) to bridge dimeric complexes has led to its wide use in systems where a close approach of two metal atoms or retention of such unit in a reaction is desired, although it displays a number of other modes of interaction.[1] Several complexes of dppm of interest in the area of compounds with metal–metal bonds have been investigated in this laboratory.[2-5] We have recently reported the synthesis and molecular structure of such complexes with group 5[17] transition metals, viz. $[VCl(dppm)BH_4]_2$[4] and $Nb_2Cl_6(dppm)_2$,[5] both of which turned out to have structures different from those expected when their preparation was undertaken. In the former, even though the dppm molecules are bridging, no metal–metal bond between vanadium atoms was present in spite of their close proximity and seemingly favorable d^3–d^3 configuration. The niobium dimer contained dppm coordinating in a chelating mode, which is unusual for this ligand in dinuclear complexes. One factor that might have been responsible for the isolation of this product was insolubility of the chelate compound relative to the desired bridged isomer. The homologue of dppm bis(dimethylphosphino)methane (dmpm) was then used in the hope that, for steric or solubility reasons, the desired bridged structure might be obtained. In this we were successful, and the first unequivocally characterized dinuclear complex of niobium or tantalum in oxidation state +3 spanned by two bidentate ligands has been obtained. To compare directly the bonding in the two diphosphinomethane derivatives, $[VCl(dmpm)BH_4]_2$ was also prepared and its structure is reported here.

Experimental Section

All operations were performed under an atmosphere of argon, with use of standard Schlenk techniques and a double-manifold vacuum line. Solvents were freshly distilled from benzophenone ketyl prior to use. Solutions were transferred via stainless cannulas and/or syringes. $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$[6] and $Nb_2Cl_6(THT)_3$[7] (THT = tetrahydrothiophene) were prepared according to the literature methods. Bis(di-

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methylphosphino)methane was purchased from Strem Chemicals, Inc., and used without further purification as a solution in hexane. A 2 M solution of $LiBH_4$ in THF was obtained from Aldrich Chemical Co.

[VCl(dmpm)BH$_4$]$_2$. A 15% v/v solution of dmpm (3 mL, ca. 3 mmol) in hexane was added to a suspension of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (0.84 g, 0.5 mmol) in 30 mL of benzene. After several hours of stirring, the suspension was blue. Addition of 4 mL of 2 M $LiBH_4$ in THF (8 mmol) resulted in a color change to purple, but only a small amount of the precipitate dissolved. The solvent was removed under vacuum and the solid material extracted with 30 mL of a 1:2 mixture of benzene/THF. Filtration afforded a black-brown solution and a black residue. Hexane was carefully layered on top of the solution, and slow interdiffusion of the solvents produced a heterogeneous solid and a red solution. The former consisted of a gray amorphous material and purple crystals. The crystals were subsequently shown to be $[VCl(dmpm)BH_4]_2$, yield ca. 0.05 g, 10%, based on vanadium.

Nb$_2$Cl$_6$(dmpm)$_2$. A 10% v/v solution of dmpm (7.5 mL, 5.5 mmol) in hexane was added to $Nb_2Cl_6(THT)_3$ (1.0 g, 1.5 mmol) in 50 mL of toluene. The color of the reaction mixture slowly changed to red, and a precipitate began to form. Stirring was continued for 1 day. Filtration afforded a red solution and a dark red precipitate (0.45 g after washing with hexane and drying). As the solution was reduced in volume, more red solid precipitated. When about 10 mL of liquid was left, 30 mL of hexane was added. An additional crop of product (0.40 g) was obtained after filtration. The solid was washed with hexane and dried under vacuum; combined yield 85%. $Nb_2Cl_6(dmpm)_2$ was unstable in solution and gradually decomposed into an as yet unidentified, insoluble green material. Excess of the decomposition product could be removed by recrystallization from toluene/hexane.

In the mass spectrum no metal-containing ions could be identified, except Nb^+. The prominent peaks were assigned as follows: 136, $[(CH_3)_2P]_2CH_2^+$ (18.5%); 121, $(CH_3)_2PCH_2P(CH_3)^+$ (9.5%); 93, Nb^+ (4.7%); 76, $(CH_3)_3P^+$ (29%); 75, $(CH_3)_2PCH_2^+$ (100%); 73, $(CH_3)_2PC^+$ (13%); 61, $(CH_3)_2P^+$ (33%).

Crystals of $Nb_2Cl_6(dmpm)_2$ were obtained by slow diffusion of the ligand (1.5 mL of a 15% v/v solution in hexane) through 20 mL of benzene/hexane (1:2) into $Nb_2Cl_6(THT)_3$ (0.2 g in 20 mL of benzene).

X-ray Crystallography. The unit cell determinations and collection of intensity data were carried out by following routine procedures used in this laboratory that have been described elsewhere.[8] Low-temperature data collection for $Nb_2Cl_6(dmpm)_2$ was done at the Molecular Structure Corp., College Station, TX. Standard computational procedures[9] were used to solve and refine structures. The intensity data were corrected for Lorentz and polarization effects before structure factors were derived. Pertinent crystallographic data for both compounds are given in Table I.

[VCl(dmpm)BH$_4$]$_2$. An empirical absorption correction based upon azimuthal scans of nine reflections near $\chi = 90°$ was applied to the intensity data.[10] The position of the vanadium atom was derived from a three-dimensional Patterson map. All non-hydrogen atoms were subsequently located by an alternating series of difference Fourier syntheses and least-squares refinements. After anisotropic displacement parameters were assigned to the atoms and the refinement was carried to convergence, the positions of the hydrogen atoms in the BH_4 ligand were derived from the difference Fourier map. The remaining hydrogen atoms were less well-defined, and no attempt was made to include them in the calculations. In subsequent full-matrix least-squares refinement of all 14 atoms the displacement parameters of H(4) had to be fixed while those of the remaining hydrogen atoms were not restrained.

Table I. Crystallographic Data

	[VCl(dmpm)BH$_4$]$_2$	Nb$_2$Cl$_6$(dmpm)$_2$[a]
formula	$V_2Cl_2P_4C_{10}B_2H_{36}$	$Nb_2Cl_6P_4C_{10}H_{28}$
fw	474.71	670.76
space group	*Pbca*	$P2_1/n$
systematic absences	$0kl,\ k \neq 2n$ $h0l,\ l \neq 2n$ $hk0,\ h \neq 2n$	$0k0,\ k \neq 2n$ $h0l,\ h + l \neq 2n$
a, Å	12.395 (3)	7.214 (3) [12.703 (6)]
b, Å	14.163 (3)	15.468 (7) [12.311 (5)]
c, Å	13.858 (4)	10.828 (5) [15.632 (5)]
α, deg	90.0	90.0 [90.0]
β, deg	90.0	93.6 (4) [90.0]
γ, deg	90.0	90.0 [90.0]
V, Å^3	2433 (2)	1205 (2) [2444 (3)]
Z	4	2 [4]
d_{calcd}, g/cm^3	1.296	1.847 [1.822]
cryst size, mm	0.3 × 0.25 × 0.1	0.15 × 0.1 × 0.1
μ(Mo Kα), cm^{-1}	12.169	18.393
data collecn instrument	CAD-4	*e*
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)	*e*
orientation reflcns: no., range (2θ)	24, $9.2 \leq 2\theta \leq 30.0$	25, $6.4 \leq 2\theta \leq 17.6$
temp, °C	22	−105
scan method	$\omega-2\theta$	$\omega-2\theta$
data collecn range, 2θ, deg	0, 45	0, 47
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1549, 1084	1200, 740
no. of parameters refined	106	100
transmission factors: max, min	0.978, 0.839	
R[b]	0.062	0.060
R_w[c]	0.074	0.070
quality-of-fit indicator[d]	1.852	1.497
largest shift/esd, final cycle	0.02	0.18
largest peak, e/Å^3	0.411	0.691

[a] Numbers in brackets are unit cell dimensions at 22 °C. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [d] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$. [e] Same entry as for the vanadium compound.

Nb$_2$Cl$_6$(dmpm)$_2$. While the crystallographic analysis based upon intensity data collected at room temperature allowed unequivocal identification of the complex, its accurate molecular structure could not be derived. Assignment of an orthorhombic unit cell was supported by axial photographs and comparison of equivalent reflections, which showed an adequate match. However, the only rigorously absent reflections were $h00$, $h \neq 2n$, and $0kl$, $k \neq 2n$, which would imply the monoclinic symmetry $P2_1/c$. Other systematic absences were observed for reflections at high 2θ angles but in all cases violations were found at lower angles. This suggested extensive pseudosymmetry or a superlattice, which we hoped to resolve after determining positions of the atoms in the unit cell. Thus in $P2_1$ (2_1 parallel to *a*) two complete dimers were located and the symmetry could be increased by adding a *b* glide perpendicular to *a*. While the positions of Nb, Cl, and P atoms seemed to indicate even higher symmetry, the carbon atoms did not conform. In addition, some equivalent bond distances in the independent half-dimers in the asymmetric unit cell differed markedly. Several orthorhombic space groups were tried, but no adequate refinement could be carried out without employing a disordered model. It was subsequently found that at −105 °C the symmetry of the unit cell was lower, apparently due to a phase change. A monoclinic unit cell in space group $P2_1/n$ with a volume half that of the orthorhombic one was obtained. A crystal structure without disorder was then derived from the low-temperature intensity data. Azimuthal scans of reflections at $\chi = 90°$ showed little variation of intensity, and therefore no absorption correction was applied.

The position of the niobium atom was obtained from the Patterson map. The remaining non-hydrogen atoms were located in a subsequent difference Fourier map. Full-matrix least-squares refinement of all the atoms first with isotropic and then with anisotropic displacement parameters gave residuals shown in Table I. The elongated vibration ellipsoids observed for some atoms are probably associated with the mosaic spread of the crystal.

Results

Molecular Structures. [VCl(dmpm)BH$_4$]$_2$. The positional and isotropic equivalent displacement parameters are listed in Table II. Important interatomic distances and angles are presented in Table III. The full listing of bond angles is included in the supplementary material. An ORTEP drawing of the molecule is shown in Figure 1.

The molecule of $[VCl(dmpm)BH_4]_2$ resides on a crystallographic inversion center. In general it is practically identical with

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Table II. Positional and Isotropic Equivalent Displacement Parameters (Å^2) for $[VCl(dmpm)BH_4]_2$[a,b]

atom	*x*	*y*	*z*	*B*
V	0.0308 (1)	0.0777 (1)	−0.0751 (1)	3.32 (3)
Cl	−0.1171 (2)	−0.0345 (2)	−0.0751 (2)	3.94 (5)
P(1)	0.1451 (2)	−0.0399 (2)	−0.1664 (2)	4.06 (5)
P(2)	−0.0884 (2)	0.1940 (2)	0.0136 (2)	4.18 (5)
C(1)	0.1174 (8)	−0.1651 (6)	−0.1398 (7)	4.7 (2)
C(2)	0.2925 (8)	−0.0269 (8)	−0.1539 (9)	6.6 (3)
C(3)	0.124 (1)	−0.0391 (8)	−0.2972 (7)	6.3 (3)
C(4)	−0.038 (1)	0.3182 (7)	0.0301 (9)	6.8 (3)
C(5)	−0.2220 (9)	0.2069 (8)	−0.0454 (9)	7.5 (3)
B	0.083 (1)	0.1956 (8)	−0.1873 (9)	5.5 (3)
H(1)	0.002 (6)	0.144 (6)	−0.198 (5)	5 (2)*
H(2)	0.139 (6)	0.171 (5)	−0.105 (5)	4 (2)*
H(3)	0.129 (7)	0.190 (6)	−0.266 (7)	7 (2)*
H(4)	0.030 (7)	0.267 (6)	−0.177 (5)	6*

[a] Atoms marked with an asterisk were refined isotropically. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Important Interatomic Distances (Å) and Angles (deg) for $[VCl(dmpm)BH_4]_2$[a]

	Distances		
V–V′	3.124 (2)	P(1)–C(2)	1.845 (8)
V–Cl	2.426 (2)	P(1)–C(3)	1.831 (8)
V–Cl′	2.419 (2)	P(2)–C(1)	1.833 (8)
V–P(1)	2.525 (2)	P(2)–C(4)	1.880 (8)
V–P(2)	2.532 (2)	P(2)–C(5)	1.855 (8)
V–B	2.372 (10)	B–H(1)	1.25 (7)
V–H(1)	1.98 (6)	B–H(2)	1.37 (6)
V–H(2)	1.93 (6)	B–H(3)	1.23 (8)
P(1)–C(1)	1.843 (7)	B–H(4)	1.23 (8)
	Angles		
Cl–V–Cl′	99.68 (6)	P(2)–V–B	91.1 (3)
Cl–V–P(1)	89.56 (7)	P(2)–V–H(1)	90 (2)
Cl–V–P(2)	89.12 (7)	P(2)–V–H(2)	94 (2)
Cl–V–B	131.9 (3)	H(1)–V–H(2)	67 (3)
Cl–V–H(1)	100 (2)	V–Cl–V′	80.32 (6)
Cl–V–H(2)	167 (2)	V–H(1)–B	92 (3)
Cl′–V–P(1)	90.96 (7)	V–H(2)–B	90 (3)
Cl′–V–P(2)	90.27 (7)	H(1)–B–H(2)	111 (4)
Cl′–V–B	128.4 (3)	H(1)–B–H(3)	103 (4)
Cl′–V–H(1)	160 (2)	H(1)–B–H(4)	93 (5)
Cl′–V–H(2)	93 (2)	H(2)–B–H(3)	119 (4)
P(1)–V–P(2)	178.33 (8)	H(2)–B–H(4)	113 (4)
P(1)–V–B	89.0 (3)	H(3)–B–H(4)	114 (4)
P(1)–V–H(1)	89 (2)		
P(1)–V–H(2)	87 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

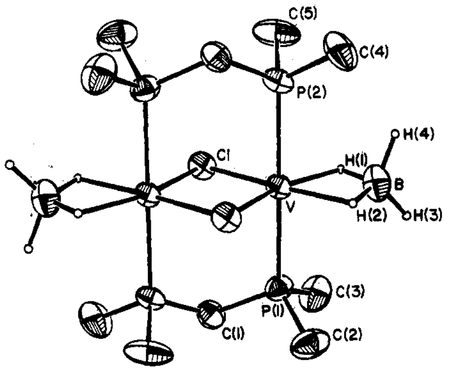


Figure 1. ORTEP drawing of the $[VCl(dmpm)BH_4]_2$ molecule. The thermal ellipsoids enclose 40% of the electron density. A crystallographic inversion center relates the halves of the molecule.

Table IV. Positional and Isotropic Equivalent Displacement Parameters (Å^2) for $Nb_2Cl_6(dmpm)_2$[a]

atom	*x*	*y*	*z*	*B*
Nb	0.0659 (3)	0.0625 (1)	0.0789 (2)	2.92 (3)
Cl(1)	−0.2528 (7)	0.0082 (3)	0.0710 (5)	2.9 (1)
Cl(2)	−0.0241 (8)	0.1271 (4)	0.2724 (5)	5.1 (1)
Cl(3)	0.3302 (8)	0.1613 (3)	0.0845 (9)	7.9 (2)
P(1)	−0.0994 (7)	0.1896 (3)	−0.0482 (5)	2.5 (1)
P(2)	0.2085 (7)	−0.0525 (3)	0.2350 (5)	2.8 (1)
C(1)	−0.287 (3)	0.152 (1)	−0.160 (2)	3.5 (5)
C(2)	−0.225 (3)	0.268 (1)	0.043 (2)	2.8 (4)
C(3)	0.052 (3)	0.259 (1)	−0.132 (2)	4.8 (6)
C(4)	0.412 (3)	−0.016 (1)	0.333 (2)	4.8 (6)
C(5)	0.047 (3)	−0.089 (1)	0.350 (2)	6.3 (7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table V. Bond Distances (Å) and Bond Angles (deg) for $Nb_2Cl_6(dmpm)_2$[a]

	Distances		
Nb–Nb′	2.711 (3)	P(1)–C(1)	1.86 (2)
Nb–Cl(1)	2.444 (4)	P(1)–C(2)	1.834 (15)
Nb–Cl(1)′	2.433 (5)	P(1)–C(3)	1.81 (2)
Nb–Cl(2)	2.446 (5)	P(2)–C(1)	1.84 (2)
Nb–Cl(3)	2.442 (5)	P(2)–C(4)	1.84 (2)
Nb–P(1)	2.641 (5)	P(2)–C(5)	1.84 (2)
Nb–P(2)	2.619 (5)		
	Angles		
Nb′–Nb–Cl(1)	56.0 (1)	Cl(3)–Nb–P(1)	82.7 (2)
Nb′–Nb–Cl(1)′	56.4 (1)	Cl(3)–Nb–P(2)	97.7 (2)
Nb′–Nb–Cl(2)	136.8 (2)	P(1)–Nb–P(2)	171.1 (2)
Nb′–Nb–Cl(3)	134.8 (2)	Nb–Cl(1)–Nb′	67.6 (1)
Nb′–Nb–P(1)	94.2 (1)	Nb–P(1)–C(1)	113.1 (5)
Nb′–Nb–P(2)	91.8 (1)	Nb–P(1)–C(2)	115.5 (6)
Cl(1)–Nb–Cl(1)′	112.4 (1)	Nb–P(1)–C(3)	115.7 (7)
Cl(1)–Nb–Cl(2)	82.5 (2)	C(1)–P(1)–C(2)	101.2 (7)
Cl(1)–Nb–Cl(3)	161.3 (2)	C(1)–P(1)–C(3)	107.4 (9)
Cl(1)–Nb–P(1)	81.1 (1)	C(2)–P(1)–C(3)	102.4 (8)
Cl(1)–Nb–P(2)	96.9 (2)	Nb–P(2)–C(1)	113.7 (6)
Cl(1)′–Nb–Cl(2)	160.6 (2)	Nb–P(2)–C(4)	115.5 (6)
Cl(1)′–Nb–Cl(3)	80.4 (2)	Nb–P(2)–C(5)	113.8 (8)
Cl(1)′–Nb–P(1)	103.8 (2)	C(1)–P(2)–C(4)	104.5 (8)
Cl(1)′–Nb–P(2)	85.1 (2)	C(1)–P(2)–C(5)	105.5 (9)
Cl(2)–Nb–Cl(3)	88.4 (2)	C(4)–P(2)–C(5)	103 (1)
Cl(2)–Nb–P(1)	90.4 (2)	P(1)–C(1)–P(2)	108.5 (8)
Cl(2)–Nb–P(2)	80.7 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

its dppm analogue[4] except for a few minor differences in bond length. In both compounds the V–V′ and V–Cl distances and corresponding angles are within esd's the same. The V–P bond lengths are a little longer in the dppm complex, which may be attributed to a more basic character of the dmpm ligand. The nonbonding V–B separation is also greater in the phenyl derivative. This is more difficult to interpret since, as is always the case in X-ray analysis, the positions of hydrogen atoms are not known with sufficient accuracy. The length of the V–V′ vector, 3.124 (2) Å, rules out any significant metal–metal bonding interaction. It is interesting to note that the P–C–P bite is almost exactly equal to the distance between the metal atoms. Since diphosphinomethane can span dimetallic units within a broad range of distances,[5] the observed match is not determined solely by the geometry of the ligand. If not incidental, it may be a result of several opposing electronic and steric factors like V–V′ repulsion, maximization of orbital overlap between V and P, and strain within the P–C–P skeleton.

$Nb_2Cl_6(dmpm)_2$. The atomic positional and isotropic equivalent displacement parameters are listed in Table IV. Bond distances and bond angles are given in Table V. The atom-labeling scheme is defined in Figure 2.

The molecule is an edge-sharing bioctahedron that resides on a crystallographic inversion center. As can be seen in Figure 3, however, the molecule of $Nb_2Cl_6(dmpm)_2$ (at least in the solid state) is distorted from the ideal edge-sharing bioctahedral geometry, in which there would be a central band of eight coplanar

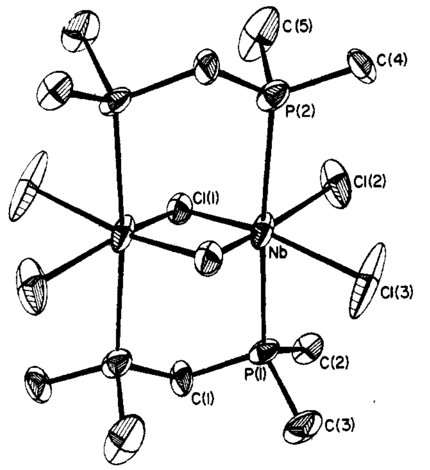


Figure 2. ORTEP drawing of the $Nb_2Cl_6(dmpm)_2$ molecule. The ellipsoids enclose 50% of the electron density. A crystallographic inversion center relates the halves of the molecule.

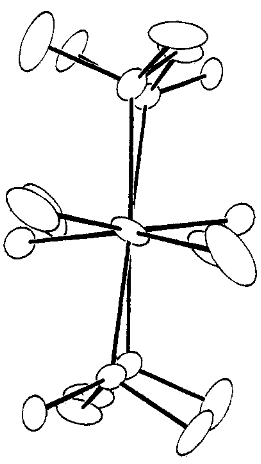


Figure 3. View of the $Nb_2Cl_6(dmpm)_2$ molecule along the metal–metal axis.

atoms. If the twist within the diphosphine is neglected, the positions of atoms connected to Nb can be approximated by three planes:[11] (1) $Nb_2(Cl_b)_2$, (2) $Nb_2(Cl_t)_4$, and (3) P_4. The dihedral angles between (1) and (2), (1) and (3), and (2) and (3) are equal: 19.3, 79.7, and 81.0°, respectively. Similar distortions are also observed in $M_2Cl_6(dppm)_2$, where M = Mo,[12] Re.[3] However, the magnitude, evaluated on the basis of appropriate torsional angles (a full listing is included in the supplementary material), is here about twice that in the other complexes. Thus, while the average displacement of the terminal chlorine atoms in $Nb_2Cl_6(dmpm)_2$ from the plane (1) is 0.56 [2] Å, in the Mo and Re complexes it is 0.234 [3] and 0.209 [4] Å, respectively. This feature, which appears to be caused by repulsions among chlorine atoms, could, of course, occur in an equivalent but opposite sense of rotation about the Nb–Nb axis. It is probable that rapid interconversion of these two directions of twist occurs in solution. Further, it may be that it is a tendency to random adoption of the two directions of twist in the crystal that leads to the change from monoclinic to orthorhombic crystal symmetry with rising temperature.

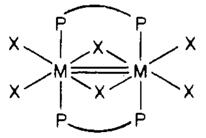
Discussion

Our goal in this work was to find out whether, in two cases[4,5] where we had previously been unsatisfied with the results obtained, the replacement of the dppm ligand by the dmpm ligand would make a difference—preferably a desirable one.

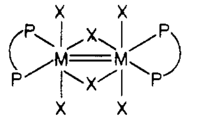
As already noted, in the case of the vanadium compound the dmpm compound is substantially identical with its dppm analogue,[4] not only in structure but also in terms of the overall chemistry involved in its preparation. Unfortunately, the preparative reaction again proceeds so as to form a considerable quantity of an amorphous byproduct, and the intended product, $[VCl(dmpm)BH_4]_2$, is similar to its dppm analogue in being subject to spontaneous decomposition in solution, with evolution of gas. This spontaneous decomposition produces a grey, amorphous solid that appears to be the same as the byproduct obtained in the previous reaction. Thus, the $V(II)/dmpm/BH_4$ system does not seem any more promising than the analogous dppm system as a route to stable compounds containing V–V bonds.

In the case of the niobium compounds substitution of dmpm made a major difference and enabled us to isolate the type of product that we had been seeking previously[5] when dppm was used. The dmpm compound has the disadvantage of being less stable than its dppm analogue; such a tendency of dmpm to give less stable products than dppm has been noted before.[13]

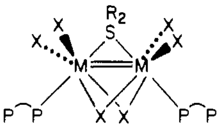
In our report[5] on the preparation and structure of $Nb_2Cl_6(dppm)_2$ we briefly considered whether a structure of type II might be inherently preferred over one of type I. We were unable to develop any conclusive arguments that favored II vs. I (or the converse, for that matter) and were forced to conclude that "we have no good explanation for the present result", i.e., for the adoption of the type II structure by $Nb_2Cl_6(dppm)_2$.



I



II



III

It is still not possible to state conclusively why the two similarly constituted products $Nb_2Cl_6(dmpm)_2$ and $Nb_2Cl_6(dppm)_2$ have the different structures I and II, respectively. On the basis of a consideration of the intermediate steps leading to the bridged complex, a kinetic/solubility kind of explanation can be proposed. The following reaction sequence is consistent with the known facts about the $M_2Cl_6(SR_2)_3/LL$ systems, where LL denotes $(R_2P)_2CH_2$:

$$M_2Cl_6(SR_2)_3 \xrightarrow[-2SR_2]{2LL} M_2Cl_6(\mu\text{-}SR_2)(LL)_2 \xrightarrow{-SR_2} M_2Cl_6(\text{chelating-}LL)_2 \rightarrow M_2Cl_6(\text{bridging-}LL)_2$$

The complex $M_2Cl_6(\mu\text{-}SR_2)(LL)_2$, with the confacial-bioctahedral structure III and monodentate dppm, has actually been isolated and its structure determined in the case of $Ta_2Cl_6(\mu\text{-}SMe_2)(dppm)_2$.[14] The elimination of the bridging SR_2 molecule might reasonably lead directly to a molecule with the type II structure. When LL = dppm, the formation of such a species is apparently followed by its immediate precipitation from the solution. In this case the usual lower solubility of complexes with chelated ligands is enhanced by the phenyl groups, which frequently give well-packed crystal lattices. No common solvent is known to reversibly dissolve $Nb_2Cl_6(dppm)_2$. It dissolves in pyridine, but on the basis of partial crystallographic characterization of the recovered material it appears that the dimer is cleaved into octahedral monomers.

We might thus propose that when LL = dppm, the very low solubility of the initially formed type II product precludes it from rearranging into the (presumably) thermodynamically favored bridging isomer, I. The use of dmpm instead of dppm provides improved solubility relationships, and the type I product with the desired coordination mode is thus obtained.

The successful preparation and structure determination of $Nb_2Cl_6(dmpm)_2$ brings to six[15] the number of edge-sharing bioctahedral structures containing two Nb(III) or two Ta(III) atoms. The M–M distances, which all presumably correspond to $\sigma^2\pi^2$ double bonds, are all within the narrow range 2.696

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[11] The table of important least-squares planes is included in the supplementary material.

[12] Chakravarty, A. R.; Cotton, F. A.; Diebold, M. P.; Lewis, D. B.; Roth, W. J. *J. Am. Chem. Soc.*, in press.

[13] King, R. B.; RaghuVeer, K. S. *Inorg. Chem.* **1984**, *23*, 2482.

[14] Cotton, F. A.; Krichbaum, G.; Meadows, J. H., unpublished results.

[15] The previous five are listed and referenced in ref 5.

(1)-2.729 (9) Å. In none of these other cases are the pairs of adjacent polar coordination sites bridged by a bidentate ligand. Nevertheless, the Nb$=$Nb distance found here, 2.711 (3) Å, is about in the middle of the previously established range. Far from being shorter than any of the others, it is third from the shortest. Thus, while the presence of a pair of bridging $R_2PCH_2PR_2$ ligands can sometimes have a dramatic effect on the M-M distance (as illustrated by the comparison of Re_2Cl_6(dppe)$_2$, which has chelating diphosphine ligands and Re···Re = 3.809 (1) Å,[16] and Re_2Cl_6(dppm)$_2$, which has bridging diphosphine ligands and Re-Re = 2.616 (1) Å[3]), this factor is not of major importance in these doubly bonded systems formed by the trivalent group 5 metals niobium and tantalum.

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Registry No. 1, 98858-56-1; **2**, 98858-57-2; $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$, 89172-48-5; $Nb_2Cl_6(THT)_3$, 98858-58-3; Nb, 7440-03-1.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic displacement parameters for both compounds, a full listing of bond angles for **1**, and listings of selected least-squares planes for **2** and torsional angles for Nb_2Cl_6(dmpm)$_2$ and M_2Cl_6(dppm)$_2$, M = Mo, Re (15 pages). Ordering information is given on any current masthead page.

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[16] Jaecker, J. A.; Robinson, W. R.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1975**, 698.

[17] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Contribution from the Department of Chemistry,
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Ferromagnetic Intramolecular Interactions in a Bis(μ-bromo)-Bridged Copper(II) Dimeric Compound: Crystal Structure and Molecular Structure Determination, Electron Paramagnetic Resonance Studies, and Magnetic Susceptibility Measurements on Bis(μ-bromo)bis[(diethylenetriamine)copper(II)] Perchlorate

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The compound bis(μ-bromo)bis[(diethylenetriamine)copper(II)] perchlorate, $[CuC_4H_{13}N_3Br]_2(ClO_4)_2$, crystallizes in the monoclinic space group $C2/c$ (C_{2h}^6, No. 15) with unit cell dimensions a = 23.054 (8) Å, b = 7.669 (1) Å, c = 14.061 (9) Å, and β = 116.02 (3)°. There are four dimers in the unit cell. The structure consists of parallel planar bis(μ-bromo)-bridged copper(II) dimers and essentially uncoordinated perchlorate anions. The geometry at each copper(II) is distorted tetragonal pyramidal with the basal ligands being three nitrogens from the diethylenetriamine ligand and one bromine, and the apical position is occupied by an inversion-related bromine atom. The dimeric unit is axial-equatorial in nature. The bridging bromide ligands are axial to one copper and equatorial to the other. The copper-bromide bond lengths are 2.424 (1) Å (equatorial) and 2.887 (1) Å (apical), and the Cu-Br-Cu′ angle is 90.63°. Analysis of temperature-dependent magnetic susceptibility data shows that the compound is ferromagnetic with a singlet-triplet splitting (ΔE_{ST}) of +2.7 cm^{-1}. EPR spectra of a powdered sample were collected at room temperature and at 77 K. EPR spectra of single crystals exhibit a strong merging effect between lines from magnetically nonequivalent dimers in the unit cell. Neither fine structure nor hyperfine structure was resolved down to 77 K. Molecular g factors of individual copper(II) ions were determined from angular dependence measurements on single crystals in a coplanar three-axial reference system to be g_z = 2.208 (1), g_y = 2.055 (1), and g_x = 2.052 (1). The line widths of the EPR lines display atypical angular dependence, i.e. $\Delta B_{pp}(\theta)$ does not reflect $g^2(\theta)$. This unusual behavior is explained in terms of an unresolved zero-field splitting resulting from intradimer dipolar coupling.

Introduction

The structural and magnetic properties of bis(μ-hydroxo) and bis(μ-chloro)-bridged complexes have been intensively studied.[4-10] Copper(II) ions in most of the bis(μ-chloro) bimetallic complexes are antiferromagnetically exchange coupled with small singlet-triplet (ΔE_{ST}) splittings,[7-9] although examples of triplet ground state, ferromagnetically coupled systems are known.[8] The singlet-triplet splittings in many of these chemically and structurally related compounds exhibit a strong correlation with the structural parameter ϕ/R, where ϕ is the Cu-Cl-Cu bridge angle and R is the longer bridge bond distance.

There is less information available about the structural and magnetic properties of bis(μ-bromo)-bridged copper(II) dimers. A correlation between the magnetic and structural characteristics of these complexes has yet to be found.

The compound formulated as Cu(dien)Br(ClO_4) (dien = diethylenetriamine) contains bis(μ-bromo)-bridged dimers in which the copper(II) ions are ferromagnetically exchange coupled. Here we describe the results of synthetic, structural, magnetic, and EPR studies on $[Cu_2(dien)_2Br_2](ClO_4)_2$.

Experimental Section

Synthesis. Diethylenetriamine, 1.1 mL (10 mmol), was added with constant stirring to a solution of 2.23 g (10 mmol) of $CuBr_2$ in 40 mL of water. Solid $NaClO_4$ (approximately 2.5 g) was added to this deep blue solution. The solution was filtered to remove any solid particles. The filtrate was left at room temperature until deep blue crystals formed (2 days). The crystals were collected by filtration, washed with ethanol and ether, and air dried. Anal. Calcd for $Cu_2(C_4H_{13}N_3)_2Br_2(ClO_4)_2$: C, 13.88; H, 3.79; N, 12.14. Found: C, 14.03; H, 3.84; N, 12.01.

X-ray Data Collection. A blue crystal of the compound was mounted at the end of a glass fiber attached to a goniometer head and was used throughout the X-ray work. The cell constants were obtained by a least-squares refinement of the setting angles of 25 reflections. The

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